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Im Auftrag

For the President of the European Patent Office

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Composition comprising anionic clay and a rare earth metal

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# COMPOSITION COMPRISING ANIONIC CLAY AND A RARE EARTH METAL

5 The present invention relates to a composition comprising anionic clay and a rare earth metal, a process for preparing this composition, and the use of this composition for catalytic purposes.

10 From the prior art it is known to use anionic clays in FCC processes, e.g. for the reduction of SOx emissions and for the reduction of the sulfur content of gasoline.

For instance, EP 0 278 535 discloses fluidizable cracking catalyst compositions containing anionic clay, the anionic clay serving as SOx binding material. Rare earth metals may be taken up in the anionic clay by coprecipitation of compounds of these metals during preparation of the  
15 anionic clay, or impregnating the anionic clay when embedded in a matrix.

WO 99/49001 discloses a composition for reducing the sulphur content of hydrocarbons, the composition comprising a hydrotalcite material that has been impregnated with a Lewis acid, selected from group of Zn, Cu, Ni, Co, Fe, Mn, lanthanides, and actinides.

20 The object of the present invention is to provide a new type of anionic clay and rare earth metal-containing composition suitable for use as SOx and NOx sorbent, for the reduction of the sulphur content of fuels, and as metal trap in FCC processes.

25 The invention relates to a composition comprising anionic clay and rare earth metal hydroxy carbonate. This composition can suitably be used in FCC processes as metal trap, for reducing of the sulfur content of gasoline and diesel, and for reducing in the SOx and NOx emissions.

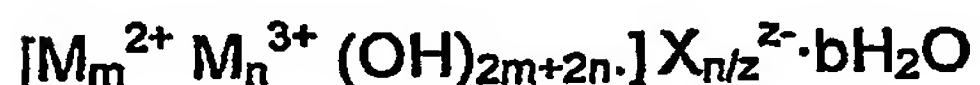
30 The invention further relates to a process for the preparation of this composition, which process comprises the steps of:

- a. precipitating a divalent metal salt, a trivalent metal salt, and a rare earth metal salt to form a precipitate,
- b. calcining the precipitate at 200-800°C, and
- c. rehydrating the precipitate in the presence of a carbonate source to form a composition comprising anionic clay and a rare earth metal hydroxy carbonate.

*The composition according to the invention*

The composition according to the invention comprises anionic clay and a rare earth metal hydroxy carbonate.

Anionic clays - also called hydrotalcite-like materials or layered double hydroxides - are materials having a crystal structure consisting of positively charged layers built up of specific combinations of divalent and trivalent metal hydroxides between which there are anions and water molecules, according to the formula



wherein  $M^{2+}$  is a divalent metal,  $M^{3+}$  is a trivalent metal, and X is an anion with valency z. m and n have a value such that  $m/n=1$  to 10, preferably 1 to 6, more preferably 2 to 4, and most preferably close to 3, and b has a value in the range of from 0 to 10, generally a value of 2 to 6 and often a value of about 4.

Hydrotalcite is an example of a naturally occurring anionic clay wherein Mg is the divalent metal, Al is the trivalent metal, and carbonate is the predominant anion present. Meixnerite is an anionic clay wherein Mg is the divalent metal, Al is the trivalent metal, and hydroxyl is the predominant anion present.

Examples of rare earth metal hydroxy carbonates are lanthanum hydroxy carbonate,  $La_2(OH)_2(CO_3)_2 \cdot H_2O$ , and cerium hydroxy carbonate,  $Ce_2(OH)_2(CO_3)_2 \cdot H_2O$ . These compounds can be identified by X-ray diffraction. The diffraction patterns of lanthanum hydroxy carbonate (JCPDS 46-0368)

and cerium hydroxy carbonate are described in *Thermochimica Acta* 137 (1989) 319-330.

5 The composition according to the invention preferably comprises 30 to 95 wt%, more preferably 40 to 90 wt%, even more preferably 40 to 85 wt%, and most preferably 40 to 70 wt% of anionic clay.

The composition preferably contains 5 to 70 wt%, more preferably 10 to 60 wt%, and even more preferably 15 to 60 wt%, and most preferably 15 to 20 wt% of the rare earth metal hydroxy carbonate.

10

The composition may contain more than one type of anionic clay and more than one type of rare earth metal hydroxy carbonate.

15 In addition to anionic clay and the rare earth metal hydroxy carbonate, the composition according to the invention may comprise other compounds, such as transition metals (e.g. V, Mo, W, Cu, Zn, Ni, Co, Fe, Mn, Fe, and/or Cr), phosphorus, other rare earth metal compounds, and/or conventional catalyst ingredients, such as matrix or filler materials (e.g. clay such as kaolin, titanium oxide, zirconia, alumina, silica, silica-alumina, bentonite, etcetera), and  
20 molecular sieve material (e.g. zeolite Y, ZSM-5, etcetera).

These metals and phosphorus can be incorporated in the compositions by, e.g., (i) co-precipitating these metals together with the divalent, trivalent, and rare earth metal salts in the first step of the preparation process according to the  
25 invention, (ii) impregnating the calcined precipitate formed as intermediate in the process according to the invention, (iii) having the metals present in the rehydration solution during the last step of the process according to the invention, or (iv) impregnating a composition comprising anionic clay and rare earth metal hydroxy carbonate.

30

The conventional catalyst ingredients can be incorporated into the composition by mixing with a composition comprising anionic clay and rare

earth metal hydroxy carbonate, or with one of the intermediates of the process according to the invention, i.e. the precipitate or the calcined precipitate. After mixing the components, the resulting mixture can be shaped to form shaped bodies. Suitable shaping methods include spray-drying, pelletising, extrusion  
5 (optionally combined with kneading), beading, or any other conventional shaping method used in the catalyst and sorbent fields or combinations thereof.

*The preparation process*

10

Precipitation

The preparation process according to the invention involves precipitation of a divalent metal salt, a trivalent metal salt, and a rare earth metal salt from a solution.

15

Suitable divalent metals include magnesium, zinc, nickel, copper, iron, cobalt, manganese, calcium, barium, strontium, and combinations thereof.

Suitable trivalent metals include aluminium, gallium, indium, iron, chromium, vanadium, cobalt, manganese, cerium, niobium, nickel, lanthanum, and  
20 combinations thereof.

Suitable rare earth metals include cerium and lanthanum.

Suitable salts of these metals are water-soluble salts, e.g. nitrates, chlorides, sulphates, acetates, formates, etc., as the precipitation is preferably conducted from aqueous solution.

25

In order to precipitate the salts, a base is added to the solution containing the dissolved salts. Any base can be used, such as NaOH, NaHCO<sub>3</sub>, NH<sub>4</sub>OH, etc., although it is preferred to use bases that do not contain sodium, as the presence of sodium is known to deteriorate the catalytic performance of many  
30 catalyst compositions, especially FCC catalyst compositions.



The pH required for precipitation depends on the metals used, but is generally above 7, preferably above 8.

5 The divalent metal, trivalent metal, and the rare earth metal can be co-precipitated together, but it is also possible to precipitate the metals in a specific order. For instance, the divalent and the trivalent metal may be precipitated first, after which the rare earth metal is precipitated. It is also possible to precipitate first the divalent and the rare earth metal, followed by precipitation of the trivalent metal, or to precipitate the trivalent and the rare  
10 earth metal, followed by precipitation of the divalent metal.

In between subsequent precipitation steps, the precipitate formed can be aged.

Examples of suitable precipitation processes can be found in European patent Application no. 0 554 968.

15

#### Calcination

The precipitate, after being isolated from the solution and optionally after washing and filtering and/or milling, is calcined at a temperature of 200-800°C, more preferably 300-700°C, and most preferably 350-600°C.  
20 Calcination is conducted for 0.25-25 hours, preferably 1-8 hours, and most preferably 2-6 hours. All commercial types of calciners can be used, such as fixed bed or rotating calciners.

Calcination can be performed in various atmospheres, e.g, in air, oxygen, inert atmosphere (e.g. N<sub>2</sub>), steam, or mixtures thereof.

25

The so-obtained calcined material must contain rehydratable oxide. The amount of rehydratable oxide formed depends on the type of divalent metal, trivalent metal, and rare earth metal used, and on the applied calcination temperature. Preferably, the calcined material contains 10-100%, more  
30 preferably 30-100%, even more preferably 50-100%, and most preferably 70-100% of rehydratable oxide.

An example of a non-rehydratable oxide is a spinel phase.

### Rehydration

Rehydration of the calcined material is conducted by contacting the calcined mixture with a polar liquid, preferably water and a carbonate source. The carbonate source can be air and/or a carbonate salt dissolved in the liquid.

Rehydration can be performed by passing the calcined mixture over a filter bed with sufficient liquid spray, or by suspending the calcined mixture in the liquid. The temperature of the liquid during rehydration is preferably between 25 and 350°C, preferably between 25 and 200°C, more preferably between 50 and 150°C, the temperature of choice depending on the nature of the anionic clay and the type and amount of metal source. Rehydration is performed for about 20 minutes to 20 hours, preferably 30 minutes to 8 hours, more preferably 1-4 hours.

During rehydration the suspension can be milled by using high-shear mixers, colloid mixers, ball mills, kneaders, electrical transducers that can introduce ultrasound waves into a slurry, etc.

Rehydration can be performed batch-wise or continuously, optionally in a continuous multi-step operation according to pre-published United States patent application no. 2003-0003035. For example, the rehydration suspension is prepared in a feed preparation vessel, whereafter the suspension is continuously pumped through two or more conversion vessels. Additional additives, acids, or bases, if so desired, can be added to the suspension in any of the conversion vessels. Each of the vessels can be adjusted to its own desirable temperature.

During rehydration, anions other than carbonate can be added to the liquid. Examples of suitable anions include inorganic anions like  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SO}_3\text{NH}_2$ ,  $\text{SCN}^-$ ,  $\text{S}_2\text{O}_6^{2-}$ ,  $\text{SeO}_4^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{BrO}_3^-$ , and  $\text{IO}_3^-$ , silicate, aluminate, and metasilicate, organic anions like acetate, oxalate, formate, long chain carboxylates (e.g. sebacate, caprate and caprylate (CPL)), alkylsulfates (e.g. dodecylsulfate (DS) and dodecylbenzenesulfate);



stearate, benzoate, phthalocyanine tetrasulfonate, and polymeric anions such as polystyrene sulfonate, polyimides, vinylbenzoates, and vinylidiacrylates, and pH-dependent boron-containing anions, bismuth-containing anions, thallium-containing anions, phosphorus-containing anions, silicon-containing anions, chromium-containing anions, vanadium-containing anions, tungsten-containing anions, molybdenum-containing anions, iron-containing anions, niobium-containing anions, tantalum-containing anions, manganese-containing anions, aluminium-containing anions, and gallium-containing anions.

10 Additionally, it is also possible to incorporate metals during rehydration, such as alkaline earth metals (for instance Mg, Ca and Ba), transition metals (for example Cr, Mn, Fe, Co, Ti, Zr, Cu, Ni, Zn, Mo, W, V, Sn, Nb), actinides, rare earth metals such as La and Ce, noble metals such as Pt and Pd, silicon, aluminium, gallium, titanium, and mixtures thereof.

15

The composition resulting from this rehydration step is the composition according to the present invention.

#### *Use of the composition*

20 The composition according to the present invention can suitably be used in or as a catalyst or catalyst additive in a hydrocarbon conversion, purification, or synthesis processes, particularly in the oil refining industry and Fischer-Tropsch processes. Examples of processes where the composition can suitably be used are fluid catalytic cracking (FCC), hydrogenation, 25 dehydrogenation, hydrocracking, hydroprocessing (hydrodenitrogenation, hydrodesulfurisation, hydrodemetallisation), polymerisation, steam reforming, base-catalysed reactions, Fischer-Tropsch, and the reduction of SO<sub>x</sub> and NO<sub>x</sub> emissions.

30 In particular, they are very suitable for use in FCC processes for the reduction of SO<sub>x</sub> and NO<sub>x</sub> emissions, reduction of the sulfur and nitrogen content of fuels like gasoline and diesel, and for entrapment of metals like V and Ni.

The product obtainable from the process according to the invention can be added to the FCC unit as such, or in a composition containing conventional catalyst ingredients, such as matrix or filler materials (e.g. clay such as kaolin, titanium oxide, zirconia, alumina, silica, silica-alumina, bentonite, etcetera),  
5 and molecular sieve material (e.g. zeolite Y, ZSM-5, etcetera).

For use as a metal trap, the composition according to the invention preferably comprises Mg-Al anionic clay; for reducing the sulphur content of fuels, Zn-Al anionic clay is preferably present; Cu-Al and Mg-Co anionic clays are  
10 preferred for reduction of NO<sub>x</sub> emissions, while Mg-Fe anionic clay is very suitable for reducing SO<sub>x</sub> emissions.

#### FIGURE

Figure 1 presents an Powder X-ray Diffraction Pattern (using Cu K-alpha  
15 radiation) of a composition according to the invention. The lines indicated with (\*) result from  $\text{La}_2(\text{CO}_3)(\text{OH})_2 \cdot \text{H}_2\text{O}$ .

09.01.2004

## CLAIMS

(95)

1. Composition comprising anionic clay and rare earth metal hydroxy carbonate.
- 5 2. Composition according to claim 1 wherein the rare earth metal is lanthanum.
- 10 3. Composition according to claim 1 wherein the anionic clay is a Mg-Al, Zn-Al, Cu-Al, Mg-Co, and/or Mg-Fe anionic clay.
- 15 4. Process for the preparation of a composition according to any one of the preceding claims, which process comprises the steps of:
  - a. precipitating a divalent metal salt, a trivalent metal salt, and a rare earth metal salt to form a precipitate,
  - b. calcining the precipitate at 200-800°C, and
  - c. rehydrating the precipitate in the presence of a carbonate source to form a composition comprising anionic clay and a rare earth metal hydroxy carbonate.
- 20 5. Use of the composition according to any one of claims 1-3 in an FCC process.
- 25 6. Use of the composition according to any one of claims 1-3 for the reduction of NO<sub>x</sub> and/or SO<sub>x</sub> emissions.
7. Use of the composition according to any one of claims 1-3 for the reduction of the S and/or N-content in fuels.
- 30 8. Use of the composition according to any one of claims 1-3 as a metal trap in FCC.

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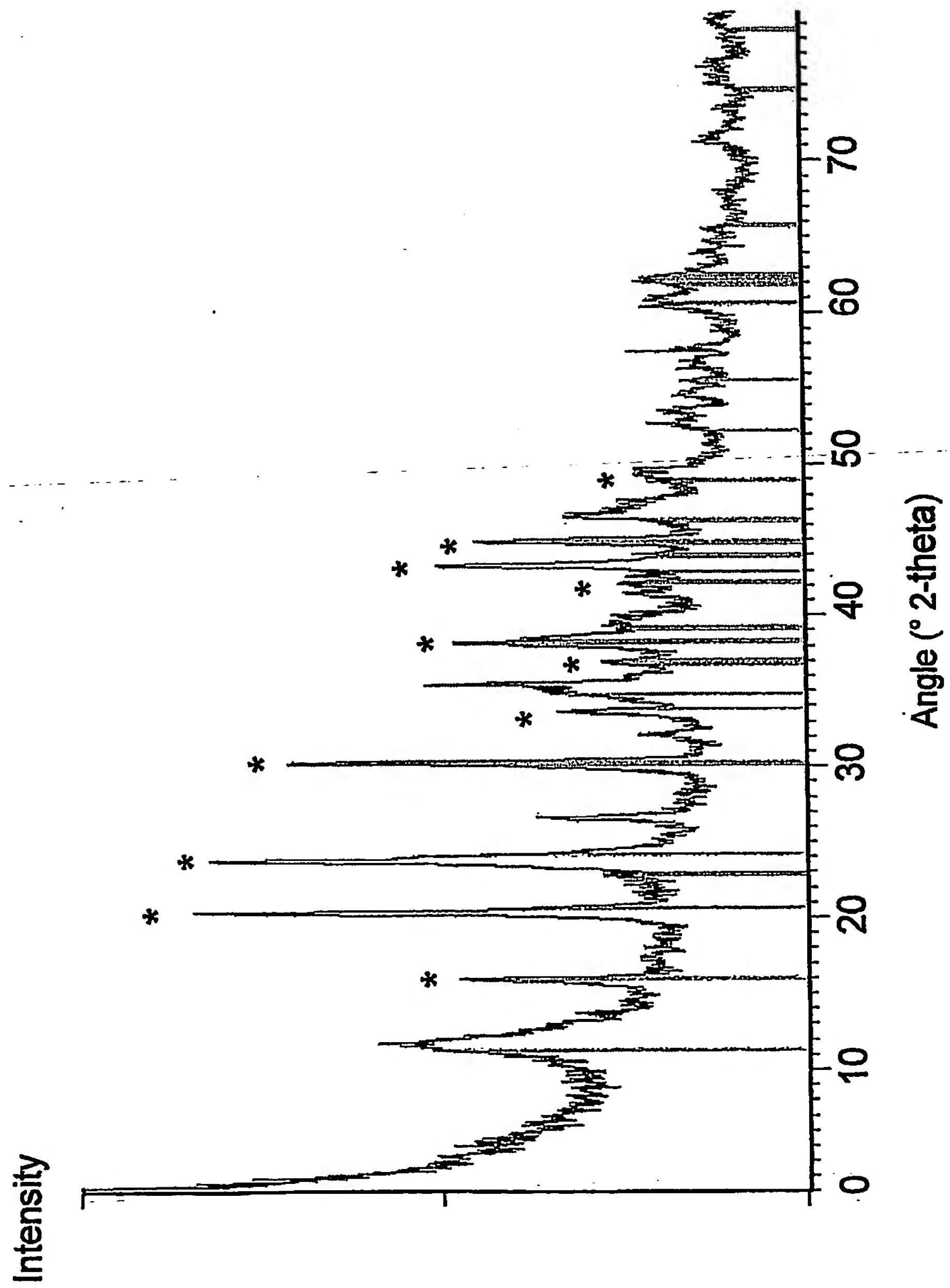
## ABSTRACT

(95)

The invention relates to a composition comprising anionic clay and rare earth metal hydroxy carbonate. This composition can suitably be used in FCC for the reduction of NO<sub>x</sub> and/or SO<sub>x</sub> emissions, the reduction of the S and/or N-content in fuels, and as a metal trap.

The composition can be prepared by precipitating a divalent metal salt, a trivalent metal salt, and a rare earth metal salt to form a precipitate, calcining the precipitate at 200-800°C, and rehydrating the precipitate in the presence of a carbonate source to form a composition comprising anionic clay and a rare earth metal hydroxy carbonate.

Figure 1/1



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